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Synthesis and characterization of palladium(II) complexes with the α-stabilized phosphoylide ligand $Ph_3P{=}C(H)CONMe_2$

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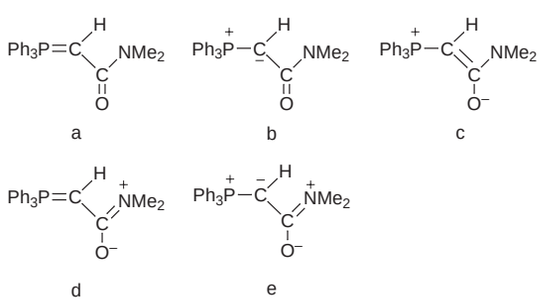
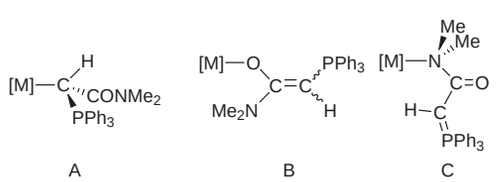
The reactivity of the ylide $Ph_3P{=}C(H)CONMe_2$ towards different palladium(II) complexes has been explored. Reaction with the cationic solvated complexes [Pd(dmba)$(NCMe)_2$]A, [Pd(*R*-dmphea)$(NCMe)_2$]A and [Pd(dmba)(py)(thf)]A (dmba = $C_6H_4CH_2NMe_2$-2; *R*-dmphea = *R*-$C_6H_4CHMeNMe_2$-2; py = pyridine; A = ClO_4^-) resulted in the formation of [Pd(dmba)(OH_2)\{CH$(CONMe_2)$$(PPh_3)$\}]A **1**, [Pd(*R*-dmphea)(OH_2)\{CH$(CONMe_2)$-(PPh_3)\}]A **2**, and [Pd(dmba)(py)\{CH$(CONMe_2)(PPh_3)$\}]A **3** respectively, in which the ylide is co-ordinated through its carbon atom, and *trans* to the NMe_2 group. The nucleophilic character of the ylidic carbon atom promotes cleavage of the halide bridging systems of the dinuclear precursors [\{Pd(μ-Br)$(\eta^3$-$C_3H_5)\}_2$], [\{Pd(μ-Cl)-(C–P)$\}_2$], [\{Pd(μ-Cl)(C_6F_5)(tht)$\}_2$], [\{Pd(μ-Cl)(dmba)$\}_2$], [\{Pd(μ-Cl)(*R*-dmphea)$\}_2$], [\{Pd(μ-Cl)[$C_6H_2(OMe)_2$-4,5-CH=NCH_2Ph-2]$\}_2$] and [\{Pd(μ-Cl)Cl$(PPh_3)\}_2$] (C–P = *o*-(di-*o*-tolylphosphino)benzyl; tht = tetrahydrothiophene), giving neutral mononuclear derivatives in which the ylide is selectively C-co-ordinated [PdBr$(\eta^3$-$C_3H_5)$-\{CH$(CONMe_2)(PPh_3)$\}] **4**, [PdCl(C–P)\{CH$(CONMe_2)(PPh_3)$\}] **5**, [PdCl(C_6F_5)(tht)\{CH$(CONMe_2)(PPh_3)$\}] **6**, [PdCl(dmba)\{CH$(CONMe_2)(PPh_3)$\}] **7**, [PdCl(*R*-dmphea)\{CH$(CONMe_2)(PPh_3)$\}] **8**, [PdCl\{$C_6H_2(OMe)_2$-4,5-CH=NCH_2Ph-2\}\{CH$(CONMe_2)(PPh_3)$\}] **9** and [$PdCl_2$$(PPh_3)$\{CH$(CONMe_2)(PPh_3)$\}] **10**. Complexes with the ylide co-ordinated through the heteroatom (oxygen or nitrogen) were not found. This selective C-co-ordination is discussed in terms of electronic and steric factors.

The α-ketostabilized phosphorus ylide $Ph_3P{=}C(H)CONMe_2$ has been found to be an interesting ligand in organometallic chemistry [1,2] and a useful intermediate for organic synthesis.[1] We have been interested recently in the chemistry of α-stabilized phosphorus ylides [3–6] $Ph_3P{=}C(H)CR$ (R = COMe, COPh, CO_2Me or CN), and have shown unambiguously the ambidentate character of these ylides as ligands in palladium(II) complexes containing C,N-cyclometalated groups. Moreover, taking into account the simple consideration of the antisymbiotic behaviour [7] of the palladium(II) centre, we have been able to predict the co-ordination mode of the ylide in a given substrate and, conversely, to design the substrate to obtain a given co-ordination mode.

The ylide $Ph_3P{=}C(H)CONMe_2$ offers new synthetic possibilities. The presence of a lone pair located on the nitrogen atom allows one to expect a new co-ordination mode, in addition to the known C- and O-co-ordination (see Schemes 1 and 2), as has been suggested.[1] We have carried out a study of the co-ordination ability of this ylide ligand towards cationic and neutral palladium(II) complexes having donor atoms *trans* to the expected co-ordination position of the ylide with different electronic and steric requirements, and in this paper we describe the results obtained. As far as we know, there is no precedent for palladium(II) complexes containing this ylide as ligand.



Scheme 1 Resonance forms for the ylide $Ph_3P{=}C(H)CONMe_2$



Scheme 2 Expected co-ordination modes for the ylide $Ph_3P{=}C(H)$-$CONMe_2$

Results and Discussion

Reactions of cationic complexes

The reaction of [\{Pd(μ-Cl)$(PR_3)_2\}_2$][ClO_4]$_2$ (PR_3 = PPh_3 or PEt_3) with 2 equivalents of ylide in deoxygenated CH_2Cl_2 under a nitrogen atmosphere at room temperature instantaneously gave deep red solutions from which the only isolated species identified was the phosphonium salt $[Ph_3PCH_2CONMe_2]^+$. The same result was observed when the starting precursor was the cationic bis(solvated) derivative [Pd(C–P)$(NCMe)_2$]ClO_4 [C–P = *o*-(di-*o*-tolylphosphino)benzyl; 1 : 1 molar ratio] even if the reaction was carried out at low temperature (183 K). The reactions with C,N-cyclometalated derivatives were more successful.

The reaction of the bis(solvated) complex [Pd(dmba)-$(NCMe)_2$]ClO_4 (dmba = $C_6H_4CH_2NMe_2$-2) with 1 equivalent of the ylide allows the isolation of a yellow solid which, after repeated recrystallization, gave pale yellow crystals whose analytical data were consistent with the stoichiometry [Pd(dmba)$(OH_2)(Ph_3PCHCONMe_2)]ClO_4$·0.5$CH_2Cl_2$ **1**·0.5-CH_2Cl_2. Attempts to obtain the corresponding solvate with NCMe {the 'expected' product [Pd(dmba)(NCMe)$(Ph_3$-$PCHCONMe_2)]ClO_4$} failed in all cases, and we are still

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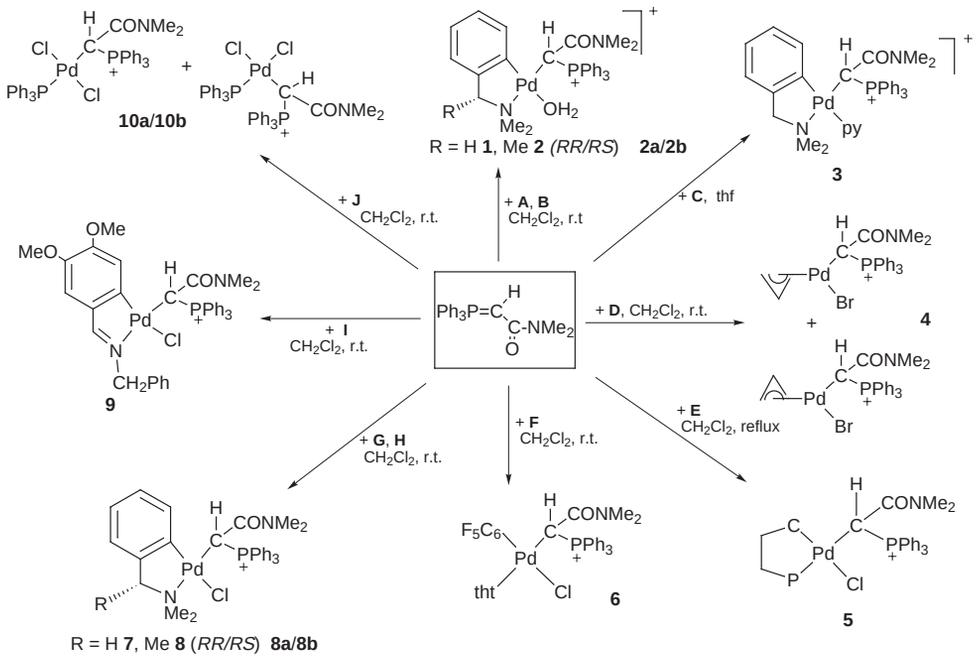
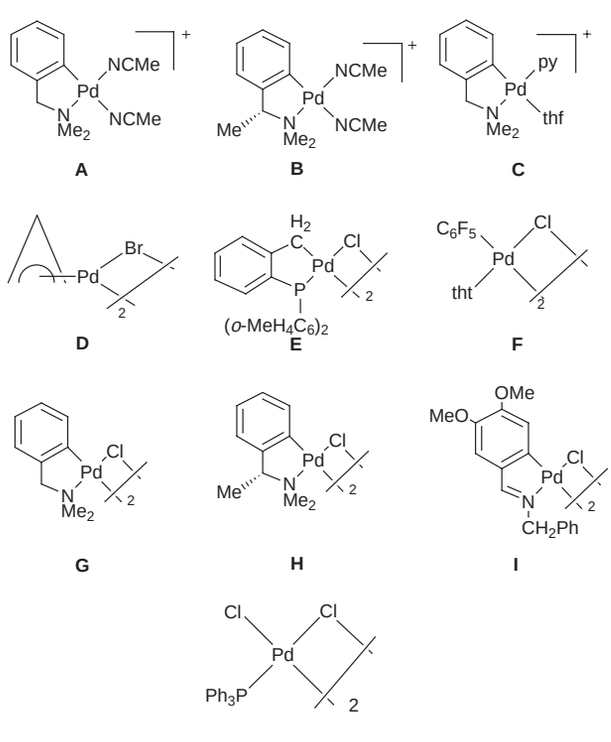


Scheme 3



unaware of the reasons for this substitution. The IR spectrum of **1** shows the absorption corresponding to the ν(CO) stretch at 1580 cm^{-1}, that is shifted to higher energies with respect to the free ylide. From our previous experience [3–6] we expect that C-co-ordination will result in a shift of the carbonyl stretch to high frequency while O-co-ordination will result in a low frequency shift. It is easy to deduce that N-co-ordination through the lone pair will also shift the carbonyl ylidic absorption to high frequency. The NMR spectra provide more structural information.

The ^{1}H NMR spectrum of complex **1** shows, in addition to the expected aromatic resonances, an AB spin system for the CH_2N protons of dmba and four singlets (relative intensity 3 : 3 : 3 : 3) corresponding to the methyl groups of the $CONMe_2$ and Pd–NMe_2 units. These facts strongly suggest C-co-ordination. Otherwise, N-co-ordination would result in the chemical equivalence of the methyl groups of each unit, and only two singlets would be observed. The ylidic proton appears at δ 3.39 as a doublet with a $^2J_{PH}$ of 4 Hz, notably smaller than that found for the free ylide (24 Hz). The ^{31}P-{^{1}H} NMR spectrum shows a single resonance at δ 27.3, shifted to low field with respect to the free ylide, and consistent with C-co-ordination. Finally, the ^{13}C-{^{1}H} NMR spectrum shows the ylidic carbon resonance shifted to high field (δ 25.76) with respect to the free ylide (δ 30.73) and as a doublet, with a value of $^1J_{PC}$ of 59 Hz, somewhat smaller than that found for the free ylide (131 Hz), and in accord with the hybridization change in the ylidic carbon ($sp^2 \longrightarrow sp^3$) in the C-co-ordination mode.

The complex [Pd(*R*-dmphea)(OH_2){CH($CONMe_2$)(PPh_3)}]ClO_4 (dmphea = $C_6H_4CHMeNMe_2$-2) **2** was synthesized similarly to **1**, and a similar substitution of the NCMe ligand by OH_2 was observed. The same conclusions can be inferred from the analysis of the IR and NMR spectra of **2** although in this case, due to the presence of the stereogenic centre in the chiral *R*-dmphea ligand, two diastereoisomers **2a** and **2b** (molar ratio major : minor = 1.75 : 1) were obtained (see Experimental section). Although a slight stereoselective induction has occurred, we have not determined unambiguously the absolute configurations of the major and minor isomers.

On the other hand, the reaction of $[Pd(dmba)(py)(thf)]^+$ with the ylide gives complex [Pd(dmba)(py){CH($CONMe_2$)(PPh_3)}]ClO_4 **3**, which shows spectral parameters in accord with the C-co-ordination mode of the ylide (see Experimental section).

Once the co-ordination mode of the ylide was established, its co-ordination position was elucidated from the determination of the crystal structure of complex **1**·0.5CH_2Cl_2 and from the ^{1}H–^{1}H NOESY spectrum measured for **3**. This spectrum shows a strong NOE interaction between the resonance at δ 3.71, attributed to the ylidic proton CH, and the resonance at δ 6.16, attributed to the proton H^6 of the dmba ligand (*ortho* to the cyclometalation position), signaling their proximity and the relative *cis* arrangement of the ylidic carbon and the cyclometalated carbon (see Scheme 3). In the same way, the saturation of the resonance at δ 2.00, attributed to one methyl group of the Pd–NMe_2 unit, results in an intense NOE effect over the resonance at δ 8.21, attributed to the H^2 proton of the pyridine ligand. This arrangement of ligands is in good agreement with

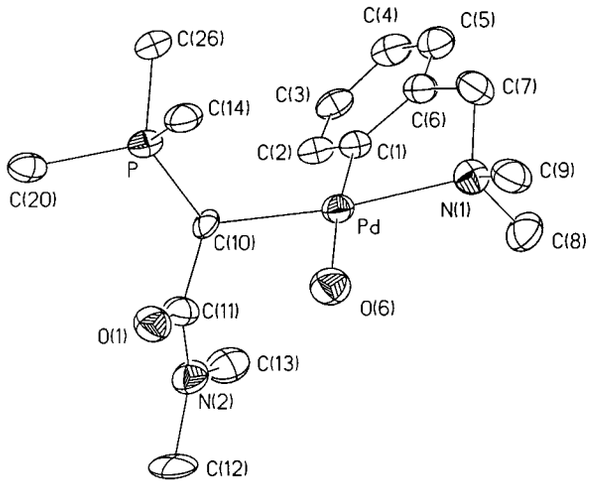


Fig. 1 Thermal ellipsoid plot of the $[Pd(dmba)(OH_2)\{CH(CONMe_2)(PPh_3)\}]^+$ cation. The Ph groups of the PPh_3 fragment (except C_{ipso}) and H atoms are omitted for clarity. Atoms are drawn at the 50% probability level

the antisymbiotic behavior of the palladium(II) centre and means that the reaction has occurred with migration of the pyridine ligand from the position *cis* to the orthometalated carbon in the starting product $[Pd(dmba)(py)(thf)]ClO_4$ to the *trans* position in **3**. This behavior has been observed previously in the chemistry of the ylide $Ph_3P{=}C(H)C(O)OMe$.[3]

Crystals of sufficient quality for X-ray analysis were grown by slow diffusion of *n*-hexane into a saturated CH_2Cl_2 solution of complex **1** at room temperature. A drawing of the organometallic cationic fragment is shown in Fig. 1, and selected bond distances and angles are collected in Table 1. The palladium atom is located in a slightly distorted square-planar environment, surrounded by the C and N atoms of the dmba ligand, the ylidic carbon atom and the oxygen atom of the water ligand. The geometrical parameters for the dmba are in the usual ranges of bond distances and angles for this ligand.[3–6] The Pd–C(10) bond distance [2.113(6) Å] is similar, within experimental error, to that found in the related complex $[Pd(dmba)(py)\{CH(COOMe)(PPh_3)ClO_4$[3] [2.098(3) Å] and is shorter than other Pd–C (ylide) bond distances found in the literature,[8–10] although all of them fall in the usual range of σ(Pd–C) distances.[11] The environment of C(10) is tetrahedral, as can be deduced from the angles given in Table 1 and, although Fig. 1 only shows one of the two enantiomers, the crystal as a whole is racemic since the space group ($P2_1/c$) is centrosymmetric. Most of the aqua complexes of palladium(II) characterized crystallographically to date have shown very similar Pd–O bond distances [range 2.106(4)–2.141(3) Å for those structures determined with reasonable accuracy[12]], regardless of the nature of the *trans* ligand and the presence or absence of hydrogen bonds between the aqua ligand and the counter ion. Thus, the Pd–O(6) bond distance in complex **1** falls out of this range [2.200(5) Å]. A similar situation has been observed in the complexes $[2\text{-}(H_2O)\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}PdTeB_{10}H_9(PPh_3)]BF_4$ [2.208(4) Å][13] and *trans*-$[PdH\{P(C_6H_{11})_3\}_2(OH_2)]BF_4$ [2.206(5) Å].[14] A sensible explanation proposed in these cases for the elongation of the Pd–O bond is the location of the aqua ligand *cis* to two very bulky groups (and so, between them), impeding an optimal metal–ligand interaction. Similar reasoning can be applied in our case, due to the location of the aqua ligand *cis* to a bulky C-co-ordinated ylide and to the NMe_2 unit of the dmba ligand, whose steric requirements have already been demonstrated.[6] Finally, it is worth noting that the environment around C(11) and N(2) is planar [Σ(angles) ≈ 360°], that the bond distance C(11)–O(1) [1.252(8) Å] indicates a double bond[15] and that C(11)–N(2) [1.349(10) Å] is in the usual range found for amides[15] where a partial contribution to double-bond character C=N is postulated.

Table 1 Selected bond distances (Å) and angles (°) for compound **1**·0.5CH_2Cl_2

Pd–C(1)	1.987(7)	P–C(26)	1.805(7)
Pd–C(10)	2.113(6)	C(10)–C(11)	1.487(9)
Pd–N(1)	2.114(6)	C(11)–O(1)	1.252(8)
Pd–O(6)	2.200(5)	C(11)–N(2)	1.349(10)
P–C(10)	1.788(7)	N(2)–C(12)	1.454(9)
P–C(14)	1.793(7)	N(2)–C(13)	1.447(10)
C(1)–Pd–N(1)	81.6(3)	C(1)–Pd–C(10)	94.1(3)
C(10)–Pd–O(6)	91.6(2)	N(1)–Pd–O(6)	92.6(2)
C(1)–Pd–O(6)	174.3(2)	C(10)–Pd–N(1)	173.3(3)
C(11)–C(10)–P	108.6(5)	C(11)–C(10)–Pd	105.6(4)
P–C(10)–Pd	107.9(3)	O(1)–C(11)–N(2)	120.2(7)
O(1)–C(11)–C(10)	119.2(7)	C(10)–C(11)–N(2)	120.5(7)
C(11)–N(2)–C(13)	121.9(7)	C(11)–N(2)–C(12)	120.2(7)
C(12)–N(2)–C(13)	117.1(7)		

In spite of the clear reactivity observed for the aforementioned cyclometalated precursors, the reaction of $[Pd(dmba)(PPh_3)(thf)]ClO_4$ with the ylide $Ph_3P{=}C(H)CONMe_2$ (1:1 molar ratio, deoxygenated thf, N_2, 0 °C) results in the formation of deep red solutions from which, after the usual work-up, the only species identified were the phosphonium salt $[Ph_3PCH_2CONMe_2]^+$ together with very small amounts of $[\{Pd(dmba)(\mu\text{-}OH)\}_2]$. This reaction was performed with the reactivity of other ketostabilized ylides towards the same complex in mind,[3] which in the other cases resulted in the selective O-co-ordination of the ylide. In this case none of the heteroatoms is able to co-ordinate.

These results are similar to those obtained with $[\{Pd(\mu\text{-}Cl)(PR_3)_2\}_2][ClO_4]_2$ and $[Pd(C{-}P)(NCMe)_2]ClO_4$, described at the beginning of this section, clearly indicating that neither the oxygen nor the nitrogen has the ability to co-ordinate under the conditions employed with our precursors and that the high nucleophilic character of the ylidic carbon atom predominates. The lack of reactivity of this ylide towards palladium through the heteroatoms (N, O) as donor atoms seems to be related to the nature of the amide group. In fact the ability of the amide group to delocalize the negative charge of the ylidic carbon is less effective than that of the 'pure' carbonyl group in the C(O)R (R = Me, Ph, or OMe) unit. This lower delocalization ability would result in a formal increase of the negative charge at the ylidic carbon atom in the ylide $Ph_3P{=}C(H)CONMe_2$ when compared with $Ph_3P{=}C(H)COR$ (R = Me, Ph or OMe). This would not mean that there is no formal partial negative charge on the amidic oxygen atom (amides react as oxygen nucleophiles in organic synthesis), but only that, in our case, the negative charge at the ylidic carbon is higher than that at the amidic oxygen. For this reason the ylidic carbon is the only 'effective' nucleophilic centre in this ylide *vis-à-vis* co-ordination to Pd, and this is in fact what we have observed experimentally.

On the other hand, the formation of a Pd–C bond *trans* to a soft atom (P, C) in our cationic complexes is not a favourable process, this formation being stabilized only if a hard atom (N) is located at the *trans* position. Such instability of mutually *trans* carbon- and phosphorus-donor ligands is well documented[16,17] and in most cases it has been invoked and employed in important C–P and C–C coupling processes.[16,18] Unfortunately, we have not detected in our complexes evidence of C–P or C–C cross-coupling products and the isolated solids were identified as the phosphonium salt. We think that this field is worth further investigation.

Reactions of neutral complexes

The reaction of the ylide $Ph_3P{=}C(H)CONMe_2$ with the dinuclear halide-bridged complexes $[\{Pd(\mu\text{-}X)L(L')\}_2]$ **D**–**J**, (X = Cl or Br; L, L′ = monodentate or chelate ligands) in 2:1 molar

ratio in deoxygenated CH_2Cl_2, under a nitrogen atmosphere results in cleavage of the bridging system and formation of the corresponding mononuclear derivatives [PdCl{CH(CONMe$_2$)(PPh$_3$)}L(L′)], in which the ylide is selectively C-co-ordinated. In this way we have obtained complexes in which the ylide is *trans* to a carbon atom [PdCl(η^3-C_3H_5){CH(CONMe$_2$)(PPh$_3$)}] **4** (as two diastereoisomers **4a** and **4b** due to the contemporaneous presence of the prochiral allyl group and the asymmetric ylidic carbon atom, see Scheme 3), complexes in which the ylide is *trans* to a phosphorus atom [PdCl(C–P){CH(CONMe$_2$)(PPh$_3$)}] **5** [C–P = $CH_2C_6H_4P(C_6H_4Me$-*o*$)_2$-2], complexes in which the ylide is *trans* to a sulfur atom [PdCl(C_6F_5)(tht){CH(CONMe$_2$)(PPh$_3$)}] **6**, and complexes in which the ylide is *trans* to a nitrogen atom [PdCl(C–N){CH(CONMe$_2$)(PPh$_3$)}] [C–N = dmba **7**; *R*-dmphea, two diastereoisomers **8a** and **8b**; $C_6H_2(OMe)_2$-4,5-CH=NCH_2Ph-2 **9**]. The reaction of [{Pd(μ-Cl)Cl(PPh$_3$)}$_2$] with the ylide under the same conditions affords the *cis* and *trans* isomers of [PdCl$_2$(PPh$_3$)-{CH(CONMe$_2$)(PPh$_3$)}] **10a** and **10b**.

The characterization of complexes **4**–**10** was carried out using the same considerations as those used for **1**–**3**: the key indicators in the complexes are the increase of ν(CO) in the IR spectra, the lower value of the coupling constant $^2J_{PH}$ and the shift to low field of the resonance attributed to the ylidic phosphorus δ(P) in the NMR spectra (see Experimental section), as compared to the values for the free ylide. The determination of the arrangement of the ligands (that is the co-ordination position of the ylide) was determined for complex **5** on the basis of the coupling constant $^3J_{PP}$ (11.7 Hz), which indicates a *trans* disposition of the ylide and the P(C_6H_4Me-*o*)$_2$ group. Complex **6** can be constituted by a mixture of two isomers derived from the two possible cleavages of the chlorine bridge: C_6F_5 *cis* to Cl (and hence C_6F_5 *trans* to ylide) and C_6F_5 *trans* to Cl. The NMR spectra of the crude product show resonances corresponding to a single product, thus only one isomer is obtained. The ^{19}F NMR spectrum shows five resonances corresponding to the five fluorine atoms of the C_6F_5 ligand which shows hindered rotation around the Pd–C_{ipso} bond. This observation, however, does not discard the C_6F_5 *cis* to Cl isomer, since hindered rotation in this disposition is well documented.[19–22] In order to obtain more structural information the ^{1}H–^{1}H NOESY spectrum of **6** was recorded. This shows clearly that there are no NOE interactions between the α-protons of the tht ligand and the ylidic proton, nor with those of the NMe$_2$ group. This fact indicates strongly their relative *trans* disposition and, obviously, the C_6F_5 *trans* to Cl arrangement. Further evidence of this is the lack in the ^{13}C-{^{1}H} NMR spectrum of coupling between the ylidic carbon and the ^{19}F nuclei of the C_6F_5 group. Thus, the C_6F_5 group lies between the tht and the ylide ligands and is *trans* to the Cl ligand. This C_6F_5 *trans* to Cl arrangement is very common in palladium chemistry with C_6F_5 ligands.[23] Finally, the ligand arrangements in complexes **7**, **8** and **9** were deduced from their close similarity to **1**–**3**.

One of the most noteworthy results of this study is the stability of the Pd–C (ylide) bond when the precursor is neutral, irrespective of the *trans* ligand, carbon, phosphorus, sulfur, nitrogen or chlorine; all the products are stable for weeks, both in the solid state and in solution. However, we have seen that reactions with cationic precursors only gave stable Pd–C (ylide) bonds when the ylide was *trans* to a 'hard' (nitrogen) atom. It is clear that the net charge of the final complex has a relevant role in the stability of the Pd–C (ylide) bonds.

It is also worth noting the different behavior of the cationic species [Pd(C–P)(NCMe)$_2$]$^+$ and the neutral [{Pd(μ-Cl)(C–P)}$_2$] towards the same ylide. At first sight one might think that the Pd–C (ylide) bond formed *trans* to a soft atom in [Pd(C–P)-(NCMe)$_2$]$^+$ (carbon or phosphorus) must be inherently weak, since all donor atoms are soft. However, the synthesis of complexes **4** and **5** and their stability show that these bonds are stable. Taking into account this stability, the characteristics of the Pd–C (ylide) σ bond itself (almost devoid of π back-bonding)[24] allows one to suppose that this bond would be more stable in a cationic complex than in a neutral one, since the metal would be better able to accept the electron density of the carbon atom. In spite of this the actual situation is the opposite; that is, with a given substituent (*e.g.* C–P) the neutral complex is more stable than the cationic, and with a given charge (*e.g.* C–P and C–N in cationic complexes) the most stable arrangement is that which possesses the hardest ligands.

A plausible explanation for all these facts can be based on the notion that a net decrease in the positive charge of the metal makes it softer, with a preference for the softer donor atom of the ylide, that is the carbon atom. This could explain not only the enhanced stability of the neutral complexes but also the selective C-co-ordination of this ylide.

Conclusion

As a general conclusion, the ylide Ph$_3$P=C(H)CONMe$_2$ behaves as a stronger C-centred nucleophile than other keto-stabilized ylides previously studied. In organometallic complexes (cationic and neutral) it co-ordinates selectively through the carbon atom. Co-ordination through the heteroatoms was never observed. The orientation of the co-ordination follows the antisymbiotic behavior of the palladium centre, and it is possible to obtain stable products irrespective of the *trans* atom in neutral complexes.

Experimental

CAUTION: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great care.

General procedures

Solvents were dried and distilled under nitrogen before use: diethyl ether and tetrahydrofuran over benzophenone ketyl, dichloromethane over P_2O_5 and *n*-hexane and toluene over sodium. Elemental analyses were carried out on a Perkin-Elmer 2400 microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 spectrophotometer in Nujol mulls between polyethylene sheets, ^{1}H (300.13), ^{13}C-{^{1}H} (75.47), ^{19}F (282.40) and ^{31}P-{^{1}H} (121.49 MHz) NMR spectra in $CDCl_3$ solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^{1}H and ^{13}C-{^{1}H} were referenced using the solvent signal as internal standard and ^{19}F and ^{31}P-{^{1}H} externally to $CFCl_3$ and H_3PO_4 (85%) respectively. The two-dimensional ^{1}H–^{1}H NOESY experiments were performed at a measuring frequency of 300.13 MHz. The data were acquired into a 256 × 1024 matrix, and then transformed into 1024 × 1024 points using a sine window in each dimension. The mixing time was 400 ms. Mass spectra (positive-ion FAB) were recorded on a V. G. Autospec spectrometer. Molecular weight determinations were made on a Knauer vapor-pressure osmometer. The starting complexes [Pd(dmba)(NCMe)$_2$]ClO$_4$,[25] [Pd(*R*-dmphea)(NCMe)$_2$]ClO$_4$,[25] [PdCl(dmba)(py)],[26] [{Pd(μ-Br)(η^3-C_3H_5)}$_2$],[27] [{Pd(μ-Cl)-(C–P)}$_2$],[28] [{Pd(μ-Cl)(C_6F_5)(tht)}$_2$],[29] [{Pd(μ-Cl)(dmba)}$_2$],[30] [{Pd(μ-Cl)(*R*-dmphea)}$_2$],[30] [{Pd(μ-Cl)[$C_6H_2(OMe)_2$-4,5-CH=NCH$_2$Ph-2]}$_2$],[31] [{Pd(μ-Cl)Cl(PPh$_3$)}$_2$][32] and the ylide Ph$_3$P=C(H)CONMe$_2$[1] were prepared according to published methods.

Preparations

[Pd(dmba)(OH$_2$){CH(CONMe$_2$)(PPh$_3$)}]ClO$_4$ 1. To a solution of [Pd(dmba)(NCMe)$_2$]ClO$_4$ (0.175 g, 0.414 mmol) in CH_2Cl_2 (20 cm^3) was added Ph$_3$P=C(H)CONMe$_2$ (0.144 g, 0.414 mmol). The resulting solution was stirred for 1 h at room temperature and evaporated to dryness. Addition of Et$_2$O

(20 cm^3) led to a yellow solid, which was recrystallized from CH_2Cl_2–*n*-hexane giving a yellow crystalline solid identified as complex **1**·0.5CH_2Cl_2 (0.150 g, 52% yield) (Found: C, 50.16; H, 4.48; N, 4.15. Calc. for $C_{31}H_{36}ClN_2O_6PPd$·0.5CH_2Cl_2: C, 50.58; H, 4.98; N, 3.74%). IR ($\tilde{\nu}_{CO}$/cm^{-1}): 1580. Mass spectrum (positive-ion FAB): *m*/*z* (%) 587 (85), $[M - OH_2]^+$. ^{1}H NMR ($CDCl_3$): δ 7.81–7.37 (m, 15 H, Ph), 6.84–6.83 (m, 2 H, dmba), 6.62–6.58 (m, 2 H, dmba), 4.10 (d, 1 H, CH_2N, $^2J_{HH}$ = 13.6), 3.49 (d, 1 H, CH_2N), 3.42 (s, 3 H, $CONMe_2$), 3.39 (d, 1 H, CH ylide, $^2J_{PH}$ = 4.1 Hz), 2.91 (s, 3 H, $CONMe_2$), 2.71 (s, 3 H, NMe_2), 2.53 (s, 3 H, NMe_2) and 2.51 (s, 2 H, OH_2). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 27.30 (P^+Ph_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 175.02 (CO), 148.00, 146.92, 143.30, 125.40, 124.14, 122.69 (C_6H_4), 133.72 (J_{PC} = 10), 133.07, 128.84 (J_{PC} = 12), 123.72 ($^1J_{PC}$ = 87 Hz, Ph), 72.19 (CH_2N), 51.61, 49.80 (NMe_2), 38.63, 36.20 (CON*Me*$_2$) and 25.76 (d, CH ylide, $^1J_{PC}$ = 59 Hz).

[Pd(*R*-dmphea)(OH_2){$CH(CONMe_2)(PPh_3)$}]ClO_4 2. Complex **2** was synthesized similarly to **1**: [Pd(*R*-dmphea)-($NCMe)_2$]ClO_4 (0.204 g, 0.466 mmol), Ph_3P=C(H)$CONMe_2$ (0.162 g, 0.466 mmol). Yield 0.279 g (85%). It was obtained as a mixture of the two diastereoisomers **2a** and **2b** in molar ratio **2a**:**2b** = 1:1.75) (Found: C, 54.02; H, 4.88; N, 3.42. Calc. for $C_{32}H_{38}ClN_2O_6PPd$: C, 53.41; H, 5.32; N, 3.89%). IR ($\tilde{\nu}_{CO}$/cm^{-1}): 1595. Mass spectrum (positive-ion FAB): *m*/*z* (%) 601 (100), $[M - OH_2]^+$. ^{1}H NMR ($CDCl_3$): δ 7.86–7.33 (m, Ph), 6.86–6.42 (m, C_6H_4), 3.90 (q, CH dmphea minor isomer, $^3J_{HH}$ = 6.0), 3.45 (s, $CONMe_2$ minor isomer), 3.44 (d, CH ylide minor isomer, $^2J_{PH}$ = 2.5), 3.42 (d, CH ylide major isomer, $^2J_{PH}$ = 2.9), 3.39 (q, CH dmphea major isomer, $^3J_{HH}$ = 6.6 Hz), 3.32 (s, CON-Me_2 major isomer), 2.93 (s, $CONMe_2$ both isomers), 2.77 (s, NMe_2 major isomer), 2.62 (s, NMe_2 minor isomer), 2.53 (s, NMe_2 major isomer), 2.41 (s, NMe_2 minor isomer), 1.44 (d, Me of dmphea minor isomer) and 1.42 (d, Me of dmphea major isomer). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 27.82 (P^+Ph_3 major isomer) and 27.77 (P^+Ph_3 minor isomer). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 175.08 (CO minor), 174.79 (CO major), 154.94, 134.62, 133.21, 129.09, 125.20, 123.33 (C_6H_4 minor), 153.23, 134.63, 133.10, 129.09, 125.55, 122.46 (C_6H_4 major), 134.39, 133.06, 128.89, 128.73, (P^+Ph_3 major), 134.26, 132.95, 128.79, 128.63 (P^+Ph_3 minor), 74.76 (CH dmphea minor), 73.03 (CH dmphea major), 51.42, 47.74 (NMe_2 minor), 50.48, 44.70 (NMe_2 major), 39.59, 36.12 (CON*Me*$_2$ major), 38.66, 35.77 (CON*Me*$_2$ minor), 26.72, 26.04 (CH ylide, both isomers), 22.72 (Me of dmphea minor) and 16.50 (Me of dmphea major).

[Pd(dmba)(py){$CH(CONMe_2)(PPh_3)$}]ClO_4 3. To a solution of [PdCl(dmba)(py)] (0.200 g, 0.563 mmol) in deoxygenated thf (30 cm^3) and under a nitrogen atmosphere, $AgClO_4$ (0.116 g, 0.563 mmol) was added. The resulting suspension was stirred at room temperature with exclusion of light for 30 min, then filtered. The freshly prepared solution of $[Pd(dmba)(py)(thf)]^+$ was cooled to 0 °C and the ylide Ph_3P=C(H)$CONMe_2$ (0.195 g, 0.563 mmol) added. A white solid precipitated almost instantaneously, whose amount was increased by evaporation to small volume (5 cm^3) and Et_2O addition (30 cm^3). This solid was filtered off, washed with cool Et_2O (25 cm^3), air dried and identified as complex **3** (0.155 g, 51% yield) (Found: C, 56.28; H, 5.22; N, 5.52. Calc. for $C_{36}H_{39}ClN_3O_5PPd$: C, 56.40; H, 5.12; N, 5.48%). IR ($\tilde{\nu}_{CO}$/cm^{-1}): 1597. Mass spectrum (positive-ion FAB): *m*/*z* (%) 587 (31), $[M - py]^+$. ^{1}H NMR ($CDCl_3$, 253 K): δ 8.21 (d, 1 H, py, $^3J_{HH}$ = 5.0), 7.80–7.74 (m, 6 H, Ph), 7.74–7.71 (m, 1 H, py), 7.64–7.59 (m, 3 H, Ph), 7.54–7.37 (m, 7 H, 6 H, Ph + 1 H, py), 7.17 (d, 1 H, py, $^3J_{HH}$ = 5.0), 6.97 (d, 1 H, dmba, $^3J_{HH}$ = 6.5), 6.85 (m, 2 H, dmba + py), 6.53 (t, 1 H, dmba, $^3J_{HH}$ = 7.2), 6.16 (d, 1 H, dmba, $^3J_{HH}$ = 7.6), 4.04, 3.85 (2d, 2 H, CH_2N, $^2J_{HH}$ = 13.5), 3.71 (d, CH ylide, $^2J_{PH}$ = 4.3 Hz), 3.25 (s, 3 H, $CONMe_2$), 2.82 (s, 3 H, $CONMe_2$), 2.36 (s, 3 H, NMe_2) and 2.00 (s, 3 H, NMe_2). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 30.02 (P^+Ph_3). ^{13}C-{^{1}H} NMR ($CDCl_3$, 253 K): δ 173.83 (CO), 150.40, 150.15, 148.22, 147.71, 138.43, 133.97, 125.92 (2C), 125.76, 124.64, 123.08 (C_6H_4 + py), 135.00 (J_{PC} = 9.8), 133.73, 129.57 (J_{PC} = 12.0), 129.41 ($^1J_{PC}$ = 128.3, Ph), 72.92 (CH_2N), 50.76 (NMe_2), 50.01 (NMe_2), 39.92 (CON*Me*$_2$), 36.22 (CON*Me*$_2$) and 26.72 (CH ylide, $^1J_{PC}$ = 50.56 Hz).

[PdBr(η^3-C_3H_5){$CH(CONMe_2)(PPh_3)$}] 4. To a solution of [{Pd(μ-Br)(η^3-C_3H_5)}$_2$] (0.162 g, 0.354 mmol) in CH_2Cl_2 (20 cm^3) the ylide Ph_3P=C(H)$CONMe_2$ (0.246 g, 0.708 mmol) was added. The resulting solution was stirred at room temperature for 30 min, then evaporated to dryness. The oily residue was treated with Et_2O (20 cm^3) giving a yellow solid which was filtered off, washed with additional Et_2O (20 cm^3), air dried, and identified as a mixture of the diastereoisomers **4a** and **4b** in molar ratio **4a**:**4b** = 1:1.25. Yield 0.293 g (72%) (Found: C, 52.09; H, 4.99; N, 2.38. Calc. for $C_{25}H_{27}BrNOPPd$: C, 52.24; H, 4.73; N, 2.44%). IR ($\tilde{\nu}_{CO}$/cm^{-1}): 1592. ^{1}H NMR [$(CD_3)_2CO$]: δ 8.06–7.49 (m, Ph), 5.08 (m, H^5 minor), 4.53 (m, H^5 major), 4.25 (s, CH ylide major), 4.17 (s, CH ylide minor), 3.78 (d, H^4 minor, $^3J_{HH}$ = 7.0), 3.67 (d, H^4 major, $^3J_{HH}$ = 5.6), 3.49 (s, $CONMe_2$ major), 3.49 (d, H^3 both isomers), 3.28 (s, $CONMe_2$ minor), 2.78 (s, $CONMe_2$ major), 2.73 (s, $CONMe_2$ minor), 2.65 (d, H^2 major, $^3J_{HH}$ = 12.5), 2.57 (d, H^2 minor, $^3J_{HH}$ = 13.2 Hz) and 2.07 (m, H^1 both isomers). ^{31}P-{^{1}H} NMR [$(CD_3)_2CO$]: δ 29.81 (P^+Ph_3 minor) and 27.47 (P^+Ph_3 major).

[PdCl(C–P){$CH(CONMe_2)(PPh_3)$}] 5. To a suspension of [{Pd(μ-Cl)(C–P)}$_2$] (0.227 g, 0.255 mmol) in CH_2Cl_2 (20 cm^3) was added Ph_3P=C(H)$CONMe_2$ (0.221 g, 0.637 mmol), and the mixture heated at reflux temperature for 12 h. The initial suspension gradually dissolved, and after the reaction time a small amount of a yellow solid identified as unchanged [{Pd-(μ-Cl)(C–P)}$_2$] remained. The suspension was filtered, the solid discarded and the resulting pale yellow solution evaporated to dryness. The yellow solid was collected with Et_2O (30 cm^3), filtered off, washed with additional Et_2O (20 cm^3), air dried and identified as complex **5** (0.141 g, 35% yield) (Found: C, 64.85; H, 5.60; N, 1.91. Calc. for $C_{43}H_{42}ClNOP_2Pd$: C, 65.16; H, 5.34; N, 1.76%). IR ($\tilde{\nu}_{CO}$/cm^{-1}): 1603. Mass spectrum (positive-ion FAB): *m*/*z* (%) 409 (22), $[M - Cl - ylide]^+$. ^{1}H NMR ($CDCl_3$, 213 K): δ 7.91–6.57 (m, 27 H, Ph + *o*-MeC_6H_4), 4.67 (d, 1 H, CH ylide, $^2J_{PH}$ = 8.9), 3.56 (s, 3 H, $CONMe_2$), 2.88 (s, 3 H, $CONMe_2$), 2.56 (s, 3 H, *o*-*Me*C_6H_4), 2.46 (s, 3 H, *o*-*Me*C_6H_4), 2.20, 1.59 (AB spin system, 2 H, CH_2Pd, $^2J_{HH}$ = 13.3 Hz). ^{31}P-{^{1}H} NMR ($CDCl_3$, 213 K): δ 34.32 (d, C–P, $^3J_{PP}$ = 11.7) and 26.17 (d, P^+Ph_3, $^3J_{PP}$ = 11.7 Hz).

[PdCl(C_6F_5)(tht){$CH(CONMe_2)(PPh_3)$}] 6. To a solution of [{Pd(μ-Cl)(C_6F_5)(tht)}$_2$] (0.151 g, 0.190 mmol) in CH_2Cl_2 (30 cm^3) was added Ph_3P=C(H)$CONMe_2$ (0.132 g, 0.381 mmol). The resulting solution was stirred at room temperature for 24 h, then evaporated to small volume (5 cm^3). The addition of Et_2O (30 cm^3) resulted in the formation of a yellow solid, which was filtered off, air dried and identified as complex **6** (0.128 g, 45% yield) (Found: C, 51.37; H, 3.66; N, 1.86; S, 4.25. Calc. for $C_{32}H_{30}F_5NOPPdS$: C, 51.63; H, 4.06; N, 1.88; S, 4.30%). IR ($\tilde{\nu}_{CO}$/cm^{-1}): 1593. ^{1}H NMR ($CDCl_3$): δ 7.74–7.63 (m, 6 H, H_o, Ph), 7.55–7.52 (m, 3 H, H_p, Ph), 7.40–7.24 (m, 6 H, H_m, Ph), 4.99 (d, 1 H, CH ylide, $^2J_{PH}$ = 5.3 Hz), 3.61 (s, 3 H, $CONMe_2$), 2.90 (m, 2 H, tht), 2.79 (s, 3 H, $CONMe_2$), 2.69 (m, 2 H, tht) and 1.86 (m, 4 H, tht). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 32.52 (P^+Ph_3). ^{19}F NMR ($CDCl_3$): δ −114.92 (d, 1F, F_o), −123.30 (d, 1F, F_o), −161.84 (t, 1F, F_p), −162.76 (m, 1F, F_m) and −163.45 (m, 1F, F_m). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 173.79 (CO), 134.50 (d, J_{PC} = 9.7), 132.73, 128.49 (d, J_{PC} = 12.5), 123.69 (d, $^1J_{PC}$ = 87.4, PPh_3), 40.75, 37.62 (SC_4H_8), 36.27, 29.83 (NMe_2) and 21.86 (d, CH ylide, $^1J_{PC}$ = 54.8 Hz).

[PdCl(dmba){$CH(CONMe_2)(PPh_3)$}] 7. To a solution of [{Pd(μ-Cl)(dmba)}$_2$] (0.211 g, 0.382 mmol) in thf (20 cm^3) was

added $Ph_3P{=}C(H)CONMe_2$ (0.265 g, 0.764 mmol). The resulting solution was stirred at room temperature for 2 h, then evaporated to small volume (2 cm^3). Subsequent addition of Et_2O (20 cm^3) and continuous stirring gave complex **7** as a pale yellow solid, which was filtered off and air dried. Yield 0.314 g (66.5%) (Found: C, 59.44; H, 5.39; N, 4.39. Calc. for $C_{31}H_{34}ClN_2OPPd$: C, 59.72; H, 5.49; N, 4.49%). IR ($\tilde{\nu}_{CO}/cm^{-1}$): 1594. Mass spectrum (positive-ion FAB): *m*/*z* (%) 587 (23), $[M - Cl]^+$. ^1H NMR ($CDCl_3$): δ 7.89–7.23 (m, 15 H, Ph), 6.67 (d, 1 H, dmba, $^3J_{HH} = 7.1$), 6.57 (d, 1 H, dmba, $^3J_{HH} = 7.2$), 6.34–6.23 (m, 2 H, dmba), 5.14 (d, 1 H, CH ylide, $^2J_{PH} = 4.5$), 4.15 (d, 1 H, CH_2N, $^2J_{HH} = 13.3$ Hz), 3.76 (s, 3 H, $CONMe_2$), 3.19 (d, 1 H, CH_2N), 2.86 (s, 3 H, $CONMe_2$), 2.76 (s, 3 H, NMe_2) and 2.53 (s, 3 H, NMe_2). ^{31}P-{^1H} NMR ($CDCl_3$): δ 27.59 (P^+Ph_3). ^{13}C-{^1H} NMR ($CDCl_3$): δ 175.40 (CO), 146.54, 132.43, 128.62, 124.81, 122.59, 121.06 (C_6H_4), 134.52 ($J_{PC} = 9$), 132.00, 128.10 ($J_{PC} = 12$), 125.71 ($^1J_{PC} = 88.3$, Ph), 72.74 (CH_2N), 52.66, 49.38 (NMe_2), 40.81 36.33 (CON*Me*$_2$) and 16.57 (d, CH ylide, $^1J_{PC} = 54.3$ Hz).

[PdCl(*R*-dmphea){CH(CONMe$_2$)(PPh$_3$)}] 8. Complex **8** was obtained similarly to **7**: [{Pd(μ-Cl)(*R*-dmphea)}$_2$] (0.241 g, 0.415 mmol) reacted with $Ph_3P{=}C(H)CONMe_2$ (0.282 g, 0.830 mmol) in thf to give **8** as a mixture of the diastereoisomers **8a** and **8b** in molar ratio **8a**:**8b** = 1:1.37 (0.400 g, 77% yield) (Found: C, 59.60; H, 5.72; N, 4.30. Calc. for $C_{32}H_{36}ClN_2OPPd$: C, 60.29; H, 5.69; N, 4.39%). IR ($\tilde{\nu}_{CO}/cm^{-1}$): 1590. Mass spectrum (positive-ion FAB): *m*/*z* (%) 601 (43), $[M - Cl]^+$. ^1H NMR ($CDCl_3$): δ 7.90–7.21 (m, Ph), 6.67–6.57 (m, C_6H_4), 6.44–6.25 (m, C_6H_4), 5.11 (s, br, CH ylide, both isomers), 3.84 (m, CH dmphea minor isomer), 3.77 (s, $CONMe_2$ major isomer), 3.70 (s, $CONMe_2$ minor), 3.23 (m, CH dmphea major), 2.90 (s, $CONMe_2$ both), 2.80 (s, NMe_2 minor), 2.62 (s, NMe_2 major), 2.58 (s, NMe_2 major), 2.39 (s, NMe_2 minor), 1.40 (d, Me dmphea major, $^3J_{HH} = 6.4$) and 1.27 (d, Me dmphea minor, $^3J_{HH} = 6.6$ Hz). ^{31}P-{^1H} NMR ($CDCl_3$): δ 28.39 (P^+Ph_3 major) and 27.99 (P^+Ph_3 minor). ^{13}C-{^1H} NMR ($CDCl_3$): δ 175.60 (CO major), 175.51 (CO minor), 153.22, 147.73, 131.55, 125.32, 122.69, 121.94 (C_6H_4 major), 150.36, 143.49, 132.62, 126.21, 124.54, 120.70 (C_6H_4 minor) 134.46, 131.97, 128.07, 127.93 (P^+Ph_3), 74.88 (CH dmphea major), 71.41 (CH dmphea minor), 51.28, 49.59 (NMe_2 major), 49.08, 41.93 (NMe_2 minor), 40.97 (CON*Me*$_2$ both), 36.61 (CON*Me*$_2$ major), 36.52 (CON*Me*$_2$ minor), 24.10 (Me dmphea major), 17.14 (d, CH ylide minor, $^1J_{PC} = 55$), 16.49 (d, CH ylide major, $^1J_{PC} = 52$ Hz) and 11.02 (Me dmphea minor).

[PdCl{C$_6$H$_2$(OMe)$_2$-4,5-CH=NCH$_2$Ph-2}{CH(CONMe$_2$)(PPh$_3$)}] 9. To a suspension of [{Pd(μ-Cl)[$C_6H_2(OMe)_2$-4,5-CH=NCH_2Ph-2]}$_2$] (0.149 g, 0.188 mmol) in CH_2Cl_2 (30 cm^3) was added $Ph_3P{=}C(H)CONMe_2$ (0.131 g, 0.376 mmol). The initial suspension gradually dissolved and, after 30 min, the resulting clear yellow solution was evaporated to dryness. The yellow solid was collected with Et_2O (30 cm^3), air dried, and identified as complex **9** (0.240 g, 86% yield) (Found: C, 60.96; H, 4.98; N, 3.66. Calc. for $C_{38}H_{38}ClN_2O_3PPd$: C, 61.38; H, 5.15; N, 3.76%). IR ($\tilde{\nu}_{CO}/cm^{-1}$): 1614. Mass spectrum (positive-ion FAB): *m*/*z* (%) 707 (3), $[M - Cl]^+$. ^1H NMR ($CDCl_3$): δ 7.92–7.86 (m, 6 H, Ph), 7.65 (s, 1 H, HC=N), 7.43–7.42 (m, 3 H, Ph), 7.31–7.18 (m, 11 H, Ph), 6.57, 6.22 (2s, 2 H, H^3, H^6), 5.38 (d, 1 H, CH ylide, $^2J_{PH} = 5.4$), 5.37 (d, 1 H, C*H*$_2$Ph, $^2J_{HH} = 14$ Hz), 4.65 (d, 1 H, C*H*$_2$Ph), 3.71 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.34 (s, 3 H, NMe_2) and 2.85 (s, 3 H, NMe_2). ^{31}P-{^1H} NMR ($CDCl_3$): δ 26.66 (P^+Ph_3).

***cis*- and *trans*-[PdCl$_2$(PPh$_3$){CH(CONMe$_2$)(PPh$_3$)}] 10.** To a suspension of [{Pd(μ-Cl)Cl(PPh_3)}$_2$] (0.150 g, 0.170 mmol) in CH_2Cl_2 (30 cm^3) was added $Ph_3P{=}C(H)CONMe_2$ (0.118 g, 0.341 mmol), resulting in immediate dissolution of the starting materials. This solution was stirred at room temperature for 15 min, then evaporated to dryness and the residue treated with Et_2O (30 cm^3). The yellow solid was collected, washed with additional Et_2O (20 cm^3), air dried and identified as a mixture of the isomers *cis*- and *trans*-[$PdCl_2(PPh_3)${$CH(CONMe_2)(PPh_3)$}] **10a**, **10b** (molar ratio = 1:1). Yield 0.235 g (87.5%) (Found: C, 60.99; H, 4.79; N, 1.80. Calc. for $C_{40}H_{37}Cl_2NOP_2Pd$: C, 61.05; H, 4.74; N, 1.58%). IR ($\tilde{\nu}_{CO}/cm^{-1}$): 1606. ^1H NMR ($CDCl_3$): δ 7.55–7.15 (m, Ph), 5.56 (d, CH ylide-*trans*-Cl, $^2J_{PH} = 12$), 4.64 (d, CH ylide-*trans*-P, $^2J_{PH} = 12.8$, $^3J_{PH} = 4.2$ Hz), 3.58 (s, $CONMe_2$ ylide-*trans*-Cl), 3.42 (s, $CONMe_2$ ylide-*trans*-P), 2.85 (s, $CONMe_2$ ylide-*trans*-Cl) and 2.80 (s, $CONMe_2$ ylide-*trans*-P). ^{31}P-{^1H} NMR ($CDCl_3$): δ 29.10 (d, ylide-*trans*-P, $^3J_{PP} = 11$ Hz), 23.87 (s, ylide-*trans*-Cl), 23.26 (d, PPh_3-*trans*-ylide) and 22.20 (s, PPh_3-*trans*-Cl).

Crystallography

X-Ray data collection. A pale yellow, block-shaped crystal of compound **1** was mounted at the end of a quartz fibre and covered with epoxy. Geometric and intensity data were taken using normal procedures on an automated four-circle Enraf-Nonius CAD4 diffractometer. After initial indexing of the cell, axial photos were taken for the axes *a*, *b* and *c* in order to check the lattice dimensions. A possible transformation of the original monoclinic cell to orthorhombic was discarded on the basis of the absence of a mirror plane in the photo for the axis [-2 0 -1] of the monoclinic cell, which would have been one of the axes of the orthorhombic cell. The scan parameters for intensity data collection were chosen on the basis of two-dimensional (ω–θ) plots of 25 reflections. Data were collected using a variable scan-speed technique in which the weakest data were measured at the slowest scan speed. That is to say no measurement was skipped or measured rapidly because of weak diffraction. Azimuthal scans of twelve scattering vectors were used as the basis of an absorption correction. No intensity decay was observed in three monitor reflections remeasured every 3 h during data collection. Small shifts in the crystal orientation were checked by measuring three standard reflections after every 400 measurements during data collection. The cell parameters were refined to the accurately determined positions of 25 reflections ($22.6 \leqslant 2\theta \leqslant 31.5°$), each measured at four equivalent positions.

Structure solution and refinement. After data reduction, all non-hydrogen atoms of one asymmetric unit were located by an automated procedure which incorporated Patterson analysis, difference direct methods, and Fourier peak list optimization.[33] The structure was refined on F_o^2, and all positive data were used in the refinement.[34] The hydrogen atoms of the cation (except those of the OH_2 ligand, see below) were placed at idealized positions and treated as riding atoms, except for those of the methyl groups, which were first located in a local slant Fourier calculation and then refined as riding atoms with the torsion angles about the N–C (methyl) bonds treated as variables. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent parameter of its parent atom. Two points of appreciable residual electron density were located in the final difference map at positions appropriate for hydrogen atoms of the co-ordinated water molecule. However, all attempts to refine them were unsuccessful, and they were not included in the final model. The interstitial dichloromethane molecule, which was located near a crystallographic inversion center, was refined with an occupancy of 0.5, and the displacement parameters of its atoms were restrained to be similar to each other. The refinement converged with the residuals shown in Table 2. Calculations were performed on a Local Area VAX-Cluster (VAX/VMS V5.5-2) and data reduction was performed with the program XCAD4B K.[35a] Absorption correction and molecular graphics were carried out with the commercial package SHELXTL PLUS.[35b]

Table 2 Crystal data for complex **1**·0.5CH_2Cl_2

Formula	$C_{31.5}H_{37}Cl_2N_2O_6PPd$
M	747.93
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	10.2080(10)
b/Å	10.204(2)
c/Å	31.345(4)
U/Å^3	3225.0(8)
β/°	98.970(10)
Z	4
F(000)	1520
T/°C	−123(2)
λ/Å	0.710 73
D_c/g cm^{-3}	1.534
Crystal size/mm	0.45 × 0.40 × 0.10
μ/mm^{-1}	0.836
Collected reflections	6029
Unique reflections	5663 (R_{int} = 0.0649)
Variables, constraint	410, 1
*R*1	0.0616
*wR*2	0.1327
Goodness of fit	0.967
Transmission factors (minimum, maximum)	0.897, 0.966
Residual electron density/e Å^{-3}	0.765

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, goodness of fit = $[\Sigma w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{\frac{1}{2}}$, n_o = number of observations, n_p = number of parameters. Weighting scheme $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where $P = [\text{max.}\ (F_o^2; 0) + 2F_c^2]/3$

CCDC reference number 186/946.

See http://www.rsc.org/suppdata/dt/1998/1699/ for crystallographic files in. cif format.

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